SYNTHESIS & CHARACTERIZATION OF COPPER-GRAPHITE METAL MATRIX COMPOSITE BY POWDER METALLURGY ROUTE

THIS THESIS IS SUBMITTED IN THE PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF **BACHELOR OF TECHNOLOGY**

IN

METALLURGICAL AND MATERIALS ENGINEERING

BY

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(Roll No. 108MM045)

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2012

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2012

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

CERTIFICATE

This is to certify that the thesis entitled **"Synthesis & Characterization of Copper-Graphite Metal Matrix Composite by Powder Metallurgy Route"** submitted by **Sibabrata Mohanty** (108MM045) and **Abhijeet Mohanty** (108MM056) in partial fulfilment of the requirements for the award of **BACHELOR OF TECHNOLOGY** Degree in **Metallurgical and Materials Engineering** at the **National Institute of Technology, Rourkela** (Deemed University) is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

Date: 10th May, 2012

Dr. Debasis Chaira
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ABSTRACT

Copper–graphite metal matrix composites possess the properties of copper, i.e. excellent thermal and electrical conductivities, and properties of graphite, i.e. solid lubricating and small thermal expansion coefficient. They are widely used as brushes, and bearing materials because of the above properties. Copper-graphite with low percentages of graphite is also used for slip rings, switches, relays, connectors, plugs and low voltage DC machines with very high current densities. In the present investigation, attempts have been made for the fabrication of Cu-graphite MMC by conventional and spark plasma sintering (SPS) techniques. The MMCs were characterised by x-ray diffraction (XRD) and scanning electron microscopy (SEM). Different mechanical properties like density, bulk hardness and wear study were also conducted. XRD spectra show the presence of Cu, graphite and Cu_2O peaks which shows that no interaction between Cu and graphite takes place during fabrication. The presence of a weak peak of Cu_2O proves that slight oxidation of Cu takes place during sintering. It has been found that addition of graphite into copper does not result in much improvement in hardness due to the soft nature of graphite. However, 90% and 97 % of theoretical density have been obtained for conventional sintered and SPS samples respectively. Maximum Vickers hardness value of around 100 has been achieved for Cu-1 vol. % graphite MMC when it is fabricated by SPS. However, a hardness value of 65 has been obtained for the same composite when it is fabricated by conventional sintering at 900°C for 1 hour. The micrographs of Cu-graphite reflect the clean interface and good compatibility between matrix and reinforcement. From wear study, it is concluded that the wear resistance of the composite increases with increase in graphite content due to the lubricating properties of graphite. It has also been found that wear depth decreases with increase in graphite content. SPS sintered samples show higher wear resistance than conventional sintered samples.

Keywords: Metal-Matrix Composites; Copper-Graphite Composites; Powder Metallurgy; conventional sintering; Spark-Plasma Sintering; Scanning Electron Microscope; X-ray Diffractometer; Wear resistance; Hardness

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Recently new materials have taken the important position in engineering field. Those materials fulfil the demand of almost all engineering applications maintaining tremendous mechanical and physical properties. In present situation, various scientists and researchers have developed the unavoidable compatible new engineering materials. Various materials have been combined with each other and give intended properties in each and every part of the world i.e. the development of new materials give another unique property and are different from their base materials. From the ancient age, this idea has been effective for mankind. Composite materials make this concept true and reinforcement in a matrix of this material contributes enhancement properties. But, neither matrix nor reinforcement alone but only composite material can be able to fulfil the requirement. Composites are exciting materials which find increasing applications in aerospace, defence, transportation, communication, power, electronics, recreation, sporting, and numerous other commercial and consumer products. Rapid advancement in the science of the fibres, matrix materials, processing interface structure, bonding and their characteristics on the final properties of the composite have taken place in the recent years. Composites are hybrids of two or more materials such as reinforced plastics, metals or ceramics. Then the properties of a composite are superior to those of its individual constituents. In a typical glass fibre reinforced plastic composite, the strength and stiffness are provided by the glass fibres while the temperature capabilities of the composite are governed by plastic matrix. They were also used in car bodies, appliances, boats etc. because of their light weight and ease of production. Complex composite parts are made by injection moulding. Advanced composites are manufactured by using these polymers with reinforcements of stronger fibres such as carbon and Aramid. These composite have applications in aircraft, automotive industry. The limitations of the polymer matrix composites at elevated temperature can be recovered by using metal matrix composites.

Metal matrix composites (MMCs) represent a new generation engineering materials. Even though they have been recently used but they have more tremendous effect due to their useful properties like specific strength, specific stiffness, wear resistance, corrosion resistance and elastic modulus etc. Copper is mostly used as an industrial and functional metal for thermal

and electronic packaging, electrical contacts and resistance welding electrodes as it has very good electrical and thermal conductivity. However, when Cu is used as electrical contacts the mechanical properties lead to wear of the component. As graphite has very good electrical conductivity, when it is reinforced into Cu, the mechanical properties improve drastically. Graphite is a solid lubricant which reduces the wear of Cu-graphite MMC.

1.2 AIMS AND OBJECTIVES OF THE PRESENT STUDY

- Fabrication of copper-graphite composite by powder metallurgy route
- Improvement of mechanical properties of the composite by using different sintering techniques such as conventional and spark plasma sintering
- Optimization of various sintering parameters like temperature, time and pressure etc.
- Study the interface between Cu and graphite
- Study the wear characteristics of the composite

1.3 SCOPE OF THE PROJECT WORK

This project thesis contains seven chapters. The first chapter presents the importance and objectives of the present investigation. The second chapter gives a brief about the previous work that has been done by other researchers in this area. The third chapter elaborates about the experimental procedure that was followed in the present study and detail of the experimental procedure. The fourth chapter presents the results and discussions. The fifth chapter describes the conclusions and main findings of the present study. The last two chapters talk about the scope for future work and list the references used during the course of this project respectively.

1.4 METAL-MATRIX COMPOSITES (MMC)

Advanced composites based on metallic matrices have a somewhat recent history, yet the opportunities look very promising. The first MMCs were developed in the 1970s for high-performance applications using continuous fibers and whiskers for reinforcement **[1].**

Metal matrix composites (MMCs) combine both metallic properties (ductility and toughness) with ceramic properties (high strength and modulus) possess greater strength in shear and compression and high service temperature capabilities. The extensive use of MMCs in aerospace, automotive industries and in structural applications has increased over past 20 years due to the availability of inexpensive reinforcements and cost effective processing routes which give rise to reproducible properties **[2]**. The frontier zone between the matrix and reinforcement phase (interface or interphase) is an essential part of MMC. Bonding between the two phases develops from interfacial frictional stress, physical and chemical interaction and thermal stresses due to mismatch in the coefficients of thermal expansion of the matrix and reinforcement. During the design of a MMC the underlying interfacial phenomenon which governs the transmission of thermal, electrical and mechanical properties is of utmost importance **[3].**

The recent recognition that addition of ceramic reinforcements enables manipulation of physical as well as mechanical properties of MMCs has led to increasingly widespread use of these materials in electronic packaging and thermal-management applications. Recent market forecasts suggest the prospect for accelerating growth of MMC use as the materials are more widely understood and are cheap, suggesting a bright future for this class of materials.

Research and development on MMCs have increased considerably in the last 10 years due to their improved modulus, strength, wear resistance, thermal resistance and fatigue resistance and improved consistency in properties and performance in general compared to the un-reinforced matrix alloys. The reinforcements are added extrinsically or formed internally by chemical reaction. The properties of MMCs depend on the properties of matrix material, reinforcements, and the matrix-reinforcement interface **[4].**

1.4.1 MATRIX

Metallic Matrices are essential constituents for fabrication of metal-matrix composites (MMCs). The choice of matrix material depends mainly on the temperature, density, strength and cost requirements for the intended applications. Other factors, such as ductility, fatigue resistance, electrical conductivity and fracture toughness are dependent on the metal selected. One of the most important factors is the compatibility of the matrix material with the reinforcement. Compatibility in this case means that no undesirable chemical reaction will occur at the interface between the matrix and reinforcement. This reaction can sometimes lead to the formation of intermetallic compounds at the interface that may cause the unwanted and dangerous effect of transferring load to the reinforcements. Also, the reaction products may act as sites for nucleation of cracks **[1].**

The maximum mechanical property advantages MMCs often provide due to the presence of reinforcement are increased modulus, strength, and fatigue strength. However, the ductility and fracture toughness of MMCs are known to be inferior to those of the unreinforced matrix alloys, because the ductility and toughness of most ceramic reinforcements are very low. These properties are very important for any load-bearing structural applications. Therefore, it is apparent that the matrix alloys having higher ductility and fracture toughness are desirable for MMC applications **[1].**

Pure metal is usually not considered as a matrix material for MMCs, because the properties of pure metals are not attractive.

1.4.2 REINFORCEMENTS

The reinforcements are either in the form of continuous fibers or discontinuous reinforcements, such as chopped fibers, whiskers, particulates, or platelets. Metal-matrix composites can be composed of either continuous or discontinuous or a combination of both these reinforcements. The main advantage of discontinuously reinforced composites over continuous ones is that they can be fabricated using processing techniques similar to those commonly used for unreinforced matrix materials, making them more cost-effective. In addition, discontinuously reinforced composites also have better isotropic properties than continuously reinforced composites, due to the lower aspect ratio and more random orientation of the reinforcements **[1]**.

1.5 COPPER-GRAPHITE COMPOSITES

Copper-Graphite composites are an example of metal matrix composites. Basically they are a dispersion of graphite in pure copper matrix. The composite that we will be studying about has been fabricated by powder metallurgy route (PM Route).They exhibit excellent lubricating and anti-seizing properties due to the presence of graphite and good electrical conductivity due to the pure copper. But there is also the problem of poor interfacial bonding between copper and graphite. The properties of the copper-graphite composites are a function of the type and amount of graphite fiber incorporated in the composite, as well as the orientation of that fiber. We generally prefer to use low percentage of graphite content in the copper matrix. In fact the amount should be such that-

- The conductivity of pure copper is not hampered much.
- The effective lubricating properties of graphite are achieved in the final composite as most of their uses come in sliding contacts (electrical).

1.5.1 Properties

- Cu-Graphite composites typically have a coefficient of thermal expansion between 4-6 ppm/ ^{o}C (depends on the temperature).
- Cu-Graphite has a density that ranges from 7.0 to 7.5 grams/cubic centimeter (20% less than copper). Switching from molybdenum or copper-tungsten to copper-graphite can save significant weight while providing better thermal performance.
- Cu/G composites also have high resistance to thermal shock.

1.5.2 Applications

- Discontinuous pitch-based graphite fiber reinforced copper composites have been under development for semiconductor thermal management. This composite is excellent in terms of machining and brazing, which renders itself as an ideal, low cost thermal management material for high power density packaging of advanced semiconductor devices.

- Typical areas of use for graphite materials impregnated with copper are systems for transmitting electrical current. In particular these include carbon brushes used in many electric motors, in railway technology or wind turbines.

- Graphite reinforced in copper is used for making sliding electrical contacts as they have excellent conductivity and anti-seizing properties.

- Copper–graphite composites are widely used as contact strips for pantographs and collector shoes in electric railways and brushes for motor technology , which combine the properties of copper, i.e. superexcellent electrical and thermal conductivities, and properties of graphite, i.e. solid lubricating, a low friction coefficient and small thermal expansion coefficient.

Figure 1: Applications of Copper Graphite Composites: (a) Electrical Contacts; (b) Carbon Graphite Bearings; (c) Copper Graphite Brushes; (d) Electrical Cables

1.6 POWDER METALLURGY

Powder Metallurgy may be defined as the art of producing metal powders and using them to make serviceable objects. This method has gained popularity because of the high strength, ductility and toughness that can be obtained by this route. One of the outstanding uses of powder metallurgy is the combination of hard materials in a metallic matrix, which serves as the basis of cemented-carbide products. Moreover, powder metallurgy is more economical than most other manufacturing processes.

Powder Metallurgy processing involves the following steps:

1. Blending of the gas-atomized matrix alloy and reinforcement in powder form;
2. Compacting (cold pressing) the homogeneous blend to roughly 80% density;
3. Degassing the preform (which has an open interconnected pore structure) to remove volatile contaminants (lubricants and mixing and blending additives), water vapor, and gases; and
4. Consolidation by vacuum hot pressing or hot isostatic pressing.

Powder metallurgy methods involve cold pressing and sintering, or hot pressing, to produce MMCs. The matrix and the reinforcement powders are blended to produce a homogeneous distribution. The blending stage is followed by cold pressing to produce what is called a *green body*, which is about 80% dense and can be easily handled. The cold pressed green body is canned in a sealed container and degassed to remove any absorbed moisture from the particle surfaces. The final step is hot pressing, uniaxial or isostatic, to produce a fully dense composite. The hot pressing temperature can be either below or above that of the matrix alloy solidus **[5]**.

1.7 SINTERING

Sintering is essentially a process of bonding solid bodies by atomic forces. The sintering process is usually carried out at a temperature below the highest melting constituent. Sintering occurs by diffusion of atoms through the microstructure. This diffusion is caused by a gradient of chemical potential – atoms move from an area of higher chemical potential to an area of lower chemical potential. The different paths the atoms take to get from one spot to another are the sintering mechanisms.

The six common mechanisms are **[16]**:

1. Surface diffusion – Diffusion of atoms along the surface of a particle
2. Vapour transport – Evaporation of atoms which condense on a different surface
3. Lattice diffusion from surface – atoms from surface diffuse through lattice
4. Lattice diffusion from grain boundary – atom from grain boundary diffuses through lattice
5. Grain boundary diffusion – atoms diffuse along grain boundary
6. Plastic deformation – dislocation motion causes flow of matter

Also one must distinguish between densifying and non-densifying mechanisms. 1–3 above are non-densifying – they take atoms from the surface and rearrange them onto another surface or part of the same surface. These mechanisms simply rearrange matter inside of porosity and do not cause pores to shrink. Mechanisms 4–6 are densifying mechanisms – atoms are moved from the bulk to the surface of pores thereby eliminating porosity and increasing the density of the sample **[16].**

Two sintering techniques basically concern us in this project. They are:

1.7.1 Conventional Sintering

It uses the conventional uniaxial die press at certain temperature and pressure conditions in a tubular furnace in the presence of an inert gas. Holding time ranges from 45 minutes to 1 hour.

1.7.2 Spark Plasma Sintering

Spark Plasma Sintering is a new technique which takes only a few minutes to complete a sintering process compared to conventional sintering which may take hours or even days for the same. This high sintering rate is possible in SPS since high heating rates can be easily attained due to internal heating of the sample as opposed to external heating seen in case of conventional sintering. Also, sintering time is reduced in SPS due to small holding time at sintering temperature, usually 5 to 10 minutes while in conventional sintering it may extend to hours. Spark plasma sintering (SPS) uses high amperage, low voltage, pulsed DC current and uniaxial pressure to consolidate powders. The heating rates normally attained in conventional furnaces are 5 to 8°C/min which can go to a maximum of up to 10°C/min. So, to attain a temperature of 1200°C we usually require 2 to 4 hours or more whereas in SPS

heating rates exceeding 300°C/min are easily obtained hence a temperature of 1200°C can be obtained in only 4 minutes **[17].**

The spark plasma sintering technique is becoming popular due to the intrinsic advantages of the method and the enhanced material properties, as well as lower processing temperature and shorter sintering time to consolidate powders compared to conventional methods. The differences between SPS and conventional methods include process efficiency and energy savings as well as microstructural and compositional implications.

CHAPTER 2

LITERATURE REVIEW

In order to gain background knowledge on the previous work done in similar fields, various papers and journals were studied. The findings of some of the journals are enumerated below:

K. Rajkumar and S. Aravindan (2009) [6] studied microwave sintering of copper–graphite composites**.** Coarser microstructure with larger porosity is obtained by this conventional sintering process which decreases the strength, wear resistance as well. In microwave sintering, heat is generated internally within the material and the sample becomes the source of heat. The direct delivery of energy to the material through the molecular interaction, results in volumetric heating. Microwave sintering offers many advantages such as faster heating rate, lower sintering temperature, enhanced densification, smaller average grain size and an apparent reduction in activation energy in sintering. The finer microstructure with relatively smaller and round pores, resulted due to microwave heating, enhances the performance of the composite. **H. Yang et al. (2010) [7]** studied the effect of the ratio of graphite/pitch coke on the mechanical and tribological properties of copper–carbon composites**.** Addition of pitch coke in the matrix can much improve the interfacial bonding strength between carbon particles and phenolic resin (binder). The bending strength and micro-hardness of the copper–carbon composites increased with increase in the content of pitch coke and reached a maximum. The friction coefficient of copper–carbon composites increased significantly with increasing the content of pitch coke. The wear rate of composites initially decreased as the content of pitch coke increased and obtained a minimum and then ascended. **J.F. Silvain et al. (1993) [8]** studied the elastic moduli, thermal expansion and microstructure of copper-matrix composite reinforced by continuous graphite fibers. Copper-matrix composites reinforced by continuous graphite fibers (Cg) were processed by hot-pressing layers of metallic pre-pregs, each fiber within the yarns having previously been coated with copper by electroplating. Composites processed according to this procedure were evaluated by tensile testing and by determination of thermal expansion coefficients and chemical and structural characterizations of the graphite/copper interface. An electroplate coating followed by diffusion bonding was found to be a successful and original way to produce fully dense Cg/Cu laminated composites. Chromium can be added to improve the chemical bonding. **Wenlin Maa and Jinjun Lu (2010) [9]** studied the effect of surface texture on transfer layer formation and tribological behavior of copper–graphite composite**.** Metal matrix composites (MMC) containing graphite particulates usually have reduced friction under dry sliding, which is closely dependent on the formation of continuous transfer

layer on the sliding surface of counterpart. Friction and wear tests were conducted under low and high load conditions and various sliding distances to evaluate the validity of the textures and their effect on the formation of the transfer layer of Cu/Gr composite. **Haijun Zhao et al. (2006) [10]** investigated the wear and corrosion behavior of Cu–graphite composites prepared by electroforming. Cu–graphite composites were prepared by electroforming technique in an acidic sulfate bath with graphite particles in suspension. The interfacial bonding between metal matrix and particles is much strengthened and porosity is eliminated in the composites in case of electroforming. Corrosion takes place at grain boundaries rather than the interface between graphite particles and Copper matrix. Wear resistance is improved after the incorporation of graphite particles into copper matrix. **Simon Dorfman & David Fuksb (1996) [11]** studied the stability of copper segregations on Copper/Carbon Metal-matrix Composite interfaces under alloying**.** Stability of interfaces in MMCs is linked to the conditions of the formation of segregations of the metal alloy at the metal/fiber interface. It is shown that alloying of the matrix, substituting copper in the interstitial metal-metalloid solid solution, changes the value of the mixing energy and influences the volume fraction of two-dimensional segregations of copper**.** We expect that the wettability of carbon fibers by the pure copper matrix may be improved by the addition of small amounts of zirconium or iron to the matrix. **Dash, K., Ray, B.C. and Chaira, D. (2011) [12]** synthesized copper–alumina metal matrix composite by conventional and spark plasma sintering and then performed characterization. The composites fabricated by SPS route do not show any peak of cuprous oxide as sintering was carried out in vacuum atmosphere. Presence of cuprous oxides was observed in the Cu/Al_2O_3 interface in the EDS of the sample fabricated by conventional sintering in hydrogen, nitrogen and argon atmosphere. The density of composites sintered by spark plasma sintering technique is quite high as compared to the other techniques. The average micro hardness value for 5% alumina reinforced $Cu–Al_2O_3$ composite is 67.8 HV for conventionally sintered samples, whereas in the present study, nano-composites fabricated by SPS method produce an average of 124.5 HV for the same composition. **S.F. Moustafa et al. (2002) [13, 14]** studied the friction and wear of copper–graphite composites made with Cu-coated and uncoated graphite powders**.** They have shown that composites made by Cu-coated and uncoated graphite have lower wear rates and friction coefficients than those made from pure copper which can be attributed to the fact that the smeared graphite layer present at the sliding surface of the wear sample acts as a solid lubricant. **Jaroslav Kovacik et al. (2007) [15]** investigated the effect of composition on the friction coefficient of copper–graphite composites in the range of 0–50 vol. % of graphite at constant load to determine critical

graphite content above which the coefficient of friction of composite remains almost composition independent and constant. They investigated that up to critical concentration threshold of graphite the decrease of the coefficient of friction is governed by the synergic effect of graphite phase sliding properties and its spatial distribution within composite microstructure. Better homogeneity of graphite phase spatial distribution leads to lower coefficient of friction of composite. Then the coefficient of friction of composites becomes independent on the composition and corresponds probably to the dynamic coefficient of friction of used graphite material whereas the wear rate decreases.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1. SAMPLE PREPARATION

As received copper and graphite powders of 25g were mixed such that the volume fractions of graphite in the mixtures were 0% (pure copper), 1%, 3%, 5% and 10 % respectively. Then, the samples were taken and blended together properly using a pestle and mortar for 30 minutes to ensure uniform distribution of the graphite particles throughout the copper matrix. The blended samples were then cold compacted by applying a load of 700 MPa for 2 minutes in a die of 25 mm diameter.

3.2. SINTERING

The compacted pellets were taken and heated in a tubular furnace in an inert atmosphere (99.99% pure argon gas) at temperatures of 900^{o} C & 950^{o} C to densify the compacted powder samples. A heating rate of 5^{o} C/minute was maintained and the holding time for the samples was 1 hour. Pellets of 25mm diameter and 15mm thickness were obtained after sintering. The densities of the sintered samples were calculated and noted.

In another set of experiment, Cu-1 vol. % graphite and Cu – 5 vol. % graphite powders were compacted at 700°C for 5 minutes under vacuum at a heating rate of 80^{o} C/minute by spark plasma sintering technique.

3.3. DENSITY MEASUREMENT

The theoretical density of the samples was calculated. The sintered density for each of the samples was measured using Archimedes' Principle. The densification parameter was also calculated to get an idea of amount of densification.

$$\text{Densification Parameter (DP)} = \frac{\text{Sintered Density} - \text{Green Density}}{\text{Theoretical Density} - \text{Green Density}}$$

$$\text{Percentage Densification} = \frac{\text{Experimental Density}}{\text{Theoretical Density}} \times 100\%$$

3.4. X-RAY DIFFRACTION ANALYSIS

XRD was studied in **PANalytical X-ray Diffractometer**. The 2θ angle was varied from 20^o to 80^o and the scanning rate used was 3^o per minute. Copper target was used.

3.5. SEM ANALYSIS

The samples were taken for microstructural analysis using a Scanning Electron Microscope. The instrument model used was **JEOL JSM-6480LV**. According to requirement secondary and back scattered images were taken.

3.6. HARDNESS MEASUREMENT

The hardness of the composite specimens was measured by Vickers hardness tester (**LECO-LV700)**. Micro-hardness of all the samples was measured under a load of 300gf for a dwell time of 5 seconds. For each specimen at least five measurements were taken at equivalent positions of the sample.

3.7. WEAR TESTING

To study wear behavior of composite specimens ball-on-plate type wear testing instrument (Model: **DUCOM TR-208-M1**) having a hardened steel ball indenter was used. Sliding wear depth of the samples was evaluated. Tests were carried out with an applied load of 0.5kg, 2mm diameter ball, 20 rpm rotational speed for a period of 15 minutes. The wear samples were observed under SEM to have an idea about wear mechanism.

CHAPTER 4

RESULTS & DISCUSSION

4.1 ANALYSIS OF AS-RECEIVED POWDERS

The as received Cu and graphite powders were characterized by SEM to get an idea about shape and size of powder particles. Figures 2(a) & 2(b) show the microstructures of as received powders of pure copper and graphite. Micrographs indicate the dendritic structure of copper and the irregularly shaped graphite particles.

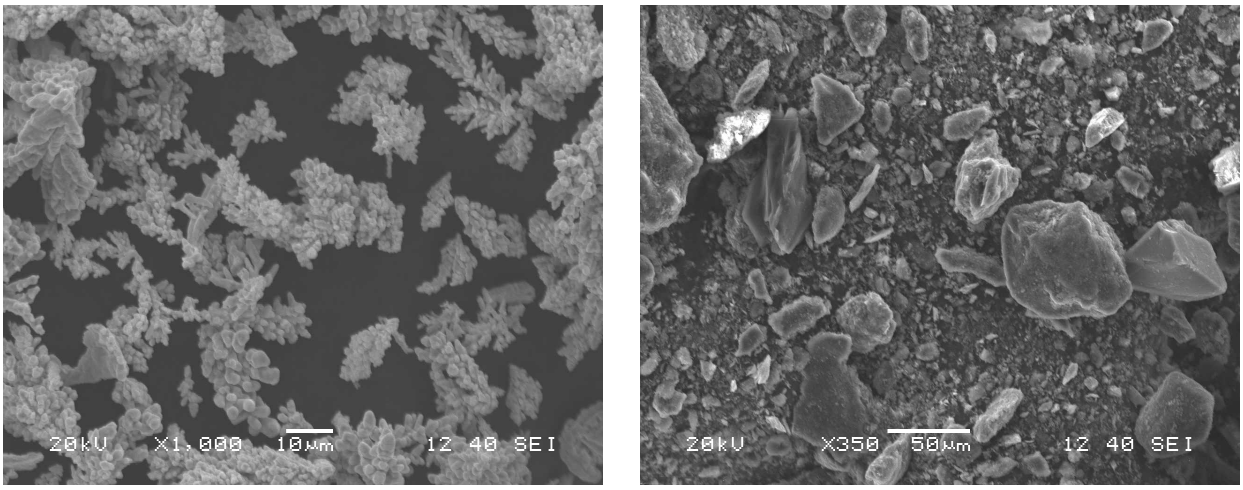

Figure 2: SEM image of as received powders of (a) Copper, (b) Graphite

Figure 3 (a) and (b) show the particle size distribution of Cu and graphite particles. It can be seen that median size for Cu is 45 microns, whereas it is 40 microns for graphite.

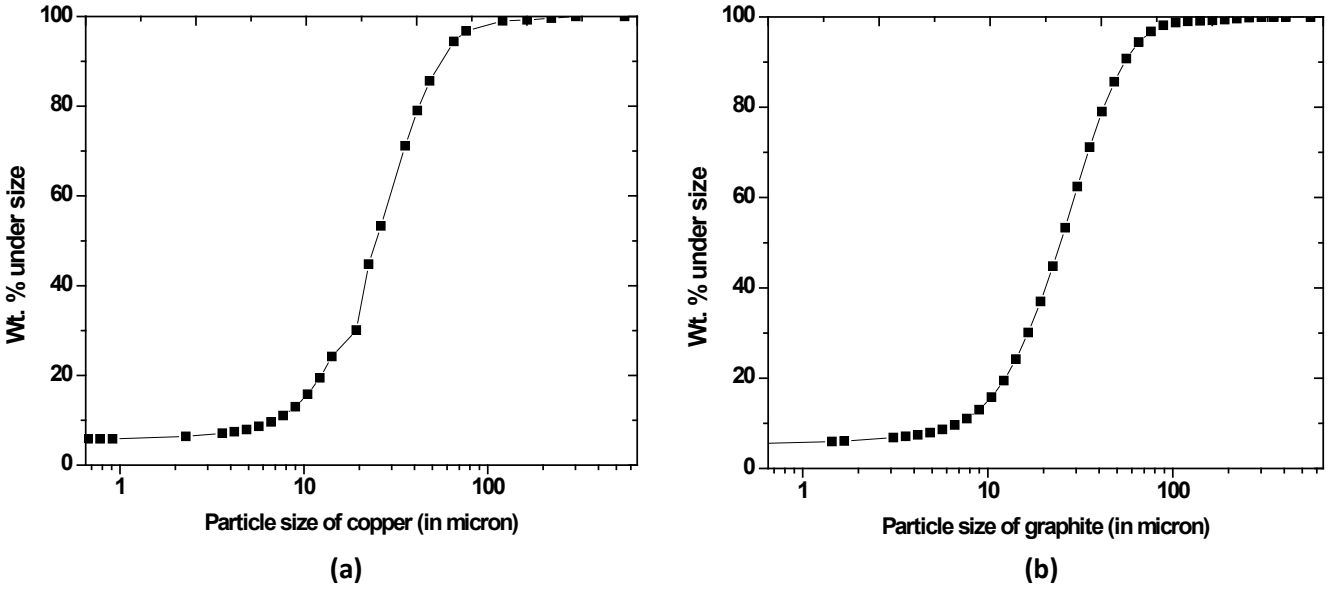

Figure 3: Size Distribution of (a) Copper, (b) Graphite Particles in the mixture

4.2 XRD ANALYSIS

XRD plots of copper-graphite composite samples with 0%, 1%, 3%, 5% & 10% by volume of graphite prepared by conventional sintering method are shown in figure 4.

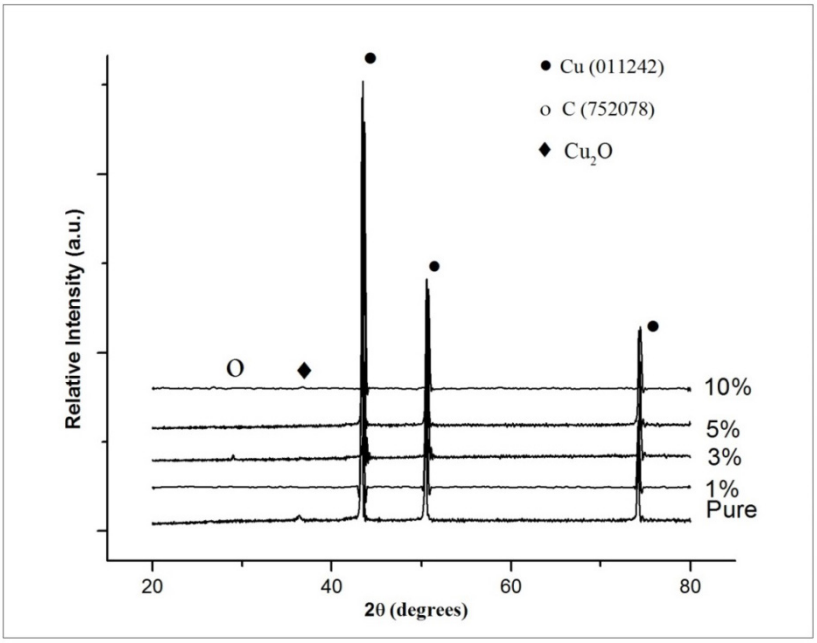

Figure 4: XRD plots of pure Cu, Cu- 1 vol. %, Cu- 3 vol. %, Cu-5 vol. % and Cu-10 vol. % graphite MMC sintered at 900°C for 1 hour

From the graph, very distinct peaks of copper can be observed. Whereas feeble peak of graphite is observed as amount of graphite is very less as compared to Cu. Also, some amount of copper oxide is detected which is undesirable. It may have been formed due to the presence of atmospheric oxygen during conventional sintering in the tubular furnace. It is also seen that no reaction takes place between copper and graphite during fabrication of composites.

Figure 5 shows the XRD spectra of Cu-1 vol. % and Cu-5 vol. % graphite MMC fabricated by spark plasma sintering at 700°C. Unlike the plots in Figure 4 where a feeble peak of copper oxide was observed, here no such formation takes place. This is due to the fact that spark plasma sintering was carried out in vacuum in the absence of atmospheric oxygen. So, oxide formation is inhibited.

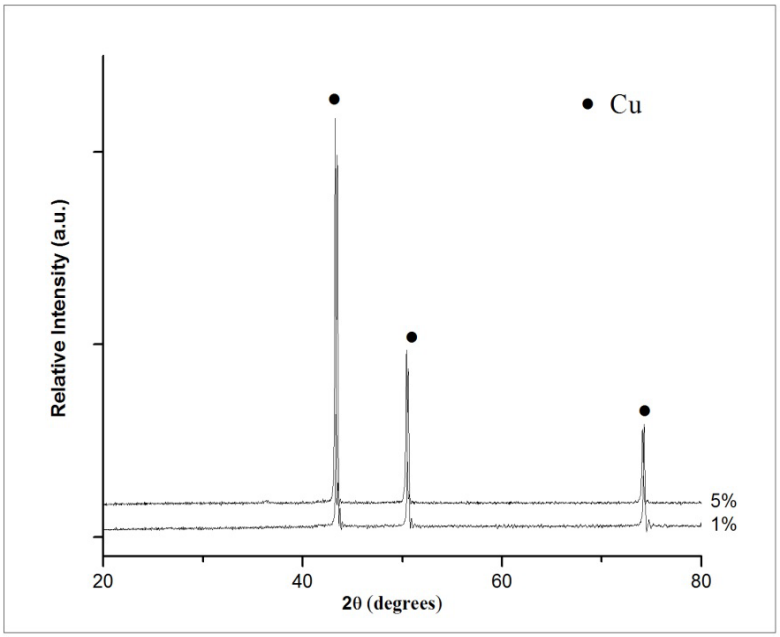

Figure 5: XRD plots of spark plasma sintered samples of 1% & 5% Graphite by volume

4.3 DENSITY MEASUREMENT

Figure 6 shows the variation of % theoretical density with volume % of graphite in the samples. Densification % increases with the increase in the volume % of graphite. This is due to the fact that the addition of graphite leads to the better encapsulation of matrix and reinforcement within the sample. The softer graphite covers up all the gaps and voids present in the original microstructure. Also the particle packing and particle–particle contact increases, between the copper and graphite at the interface. Densification Parameter also increases with graphite.

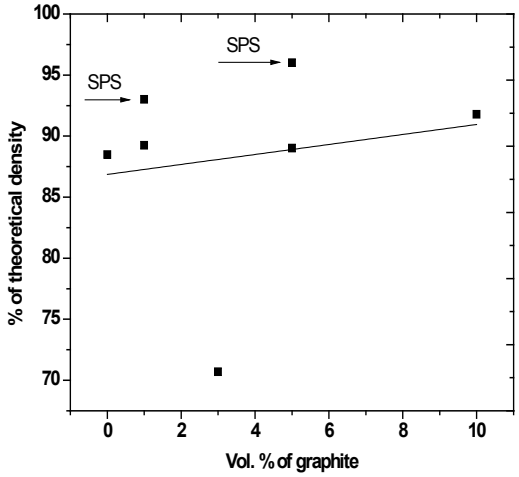

Figure 6: Variation of % theoretical density with volume % of graphite

4.4 HARDNESS MEASUREMENT

The Vickers hardness for different samples corresponding to conventionally sintered samples at 900^{o}C with graphite of 0%, 1%, 3%, 5% & 10% by volume was recorded. The same was done for spark plasma sintered samples (1% & 5% by volume of graphite). The microhardness of both set of samples was compared by plotting graphs between Vickers Hardness and varying composition of graphite.

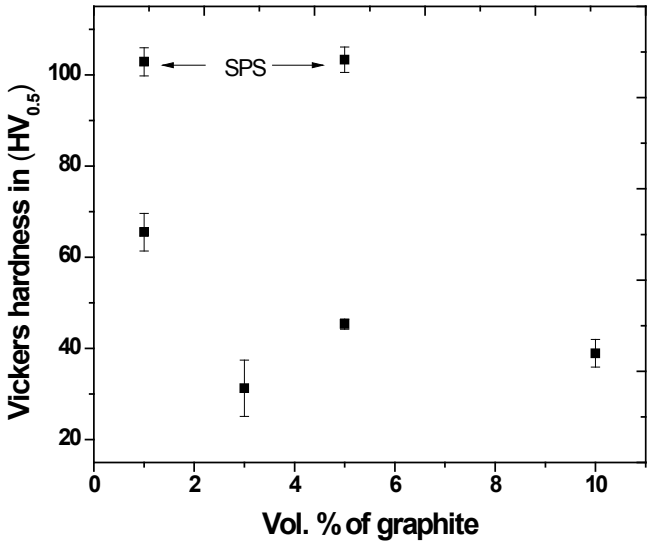

Figure 7: Variation in Vickers Hardness with volume % of graphite for conventionally sintered samples & SPS samples

The trend in the graph indicates that hardness of the conventionally sintered sample [Figure 7] increases up to the presence of about 1% graphite and then decreases. This may be due to facilitation of agglomeration of softer graphite fines after the critical concentration is reached. Another factor that may have contributed to the increase in the hardness initially is the effective dispersion strengthening by the introduction of graphite particles in the copper matrix.

As expected, the spark plasma sintered sample (Figure 7) has a much higher hardness value (in the range of 100 H_v) than the conventionally sintered sample. Better dispersion of graphite in copper matrix may have led to small-scale pinning in the composites, thus preventing grain growth and increasing hardness. Another reason for the high hardness in SPS samples may be owed to the fact that sintering occurs at high pressures that results in superior compaction. Also the hardness values of the SPS sample remains almost constant as we increase the graphite volume content from 1% to 5%.

4.5 SEM ANALYSIS

SEM images for samples having 1%, 3%, 5% & 10% by volume of graphite and ***conventionally sintered*** at 900^{o}C are shown below.

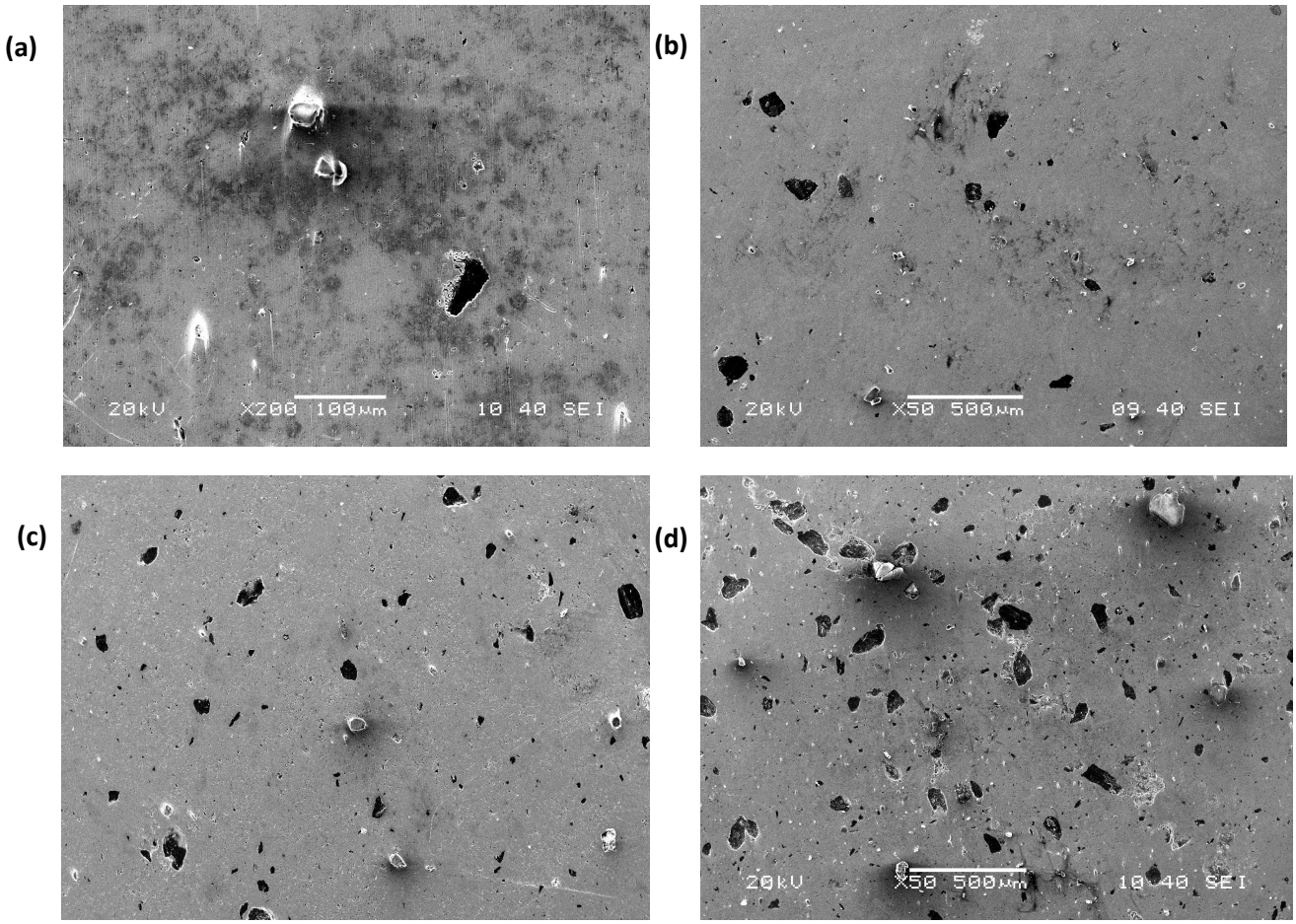

Figure 8: SEM images of conventionally sintered samples of (a) 1%, (b) 3%, (c) 5% & (d) 10% by volume of graphite

From the SEM images in Figure 8, the following observations were made: There was uniform distribution of graphite (dark regions) in the copper matrix (white regions). Also the distribution is true in the sense that at similar magnification we can see increase in number of dark regions with increase in percentage of graphite. Very less agglomeration is observed. There are few gaps observed in the copper matrix.

In Figure 9, the EDS spectra of a region in copper-5 vol. % of graphite sample are shown. Distinct copper and carbon peaks can be seen from the EDS spectra.

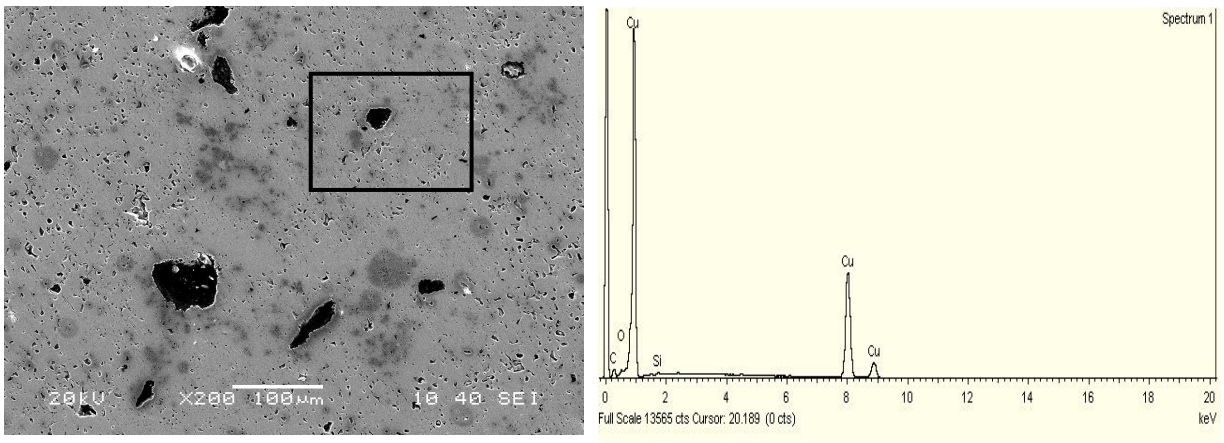

Figure 9: EDS spectra of Cu-5 vol. % graphite MMC sintered at 900°C for 1 hour

Figure 10(a) & (b) show the copper graphite interface in conventional and SPS samples. In both the cases, we can see good compatibility between the graphite and the copper matrix interface since the boundary seems continuous without any formation of voids or cracks.

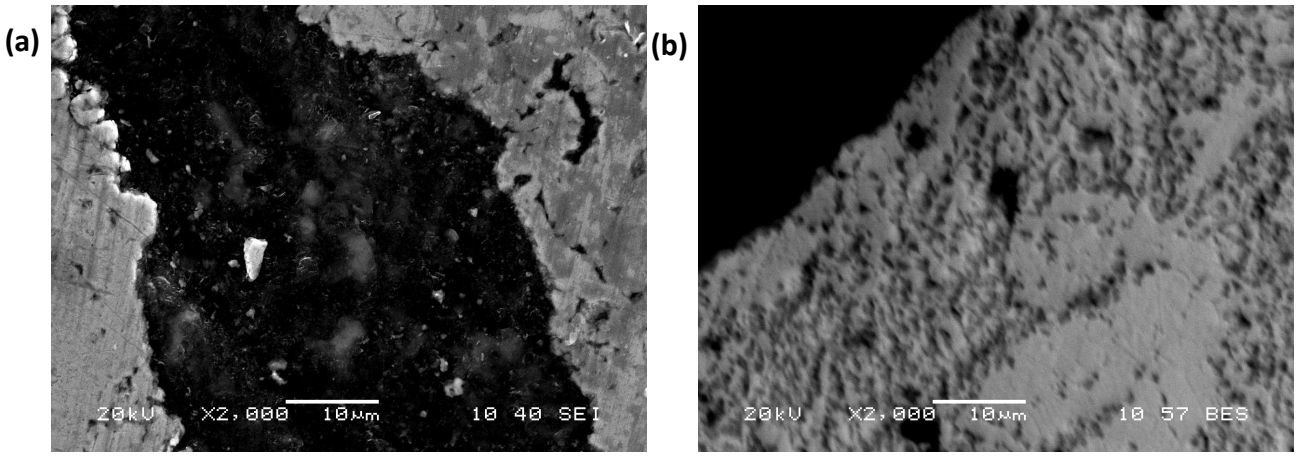

Figure 10: SEM images showing copper-graphite interface in (a) conventionally sintered, (b) spark plasma sintered samples

4.6 WEAR STUDY

Figure 11 shows the variation of wear depth with time for Cu-10 vol. % graphite (conventionally sintered), Cu-1 vol. % graphite (SPS) & Cu-5 vol. % graphite (SPS) samples. We observe a decreasing trend in wear depth with increase in volume % of graphite for SPS samples. The main reason for this could be due to the increase in thickness of smeared graphite layer at the sliding surface of the wear sample, which is generated due to the extrusion of graphite to the surface of the tested pin during sliding and which acts as a solid lubricant.

Better homogeneity of graphite phase spatial distribution leads to lower coefficient of friction of composite or better wear properties. However in conventionally sintered Cu-graphite MMC, there is high probability of clustering of graphite particles. This may be the only plausible explanation for such high wear depth of Cu-10 volume % graphite sample (even with such high graphite concentration).

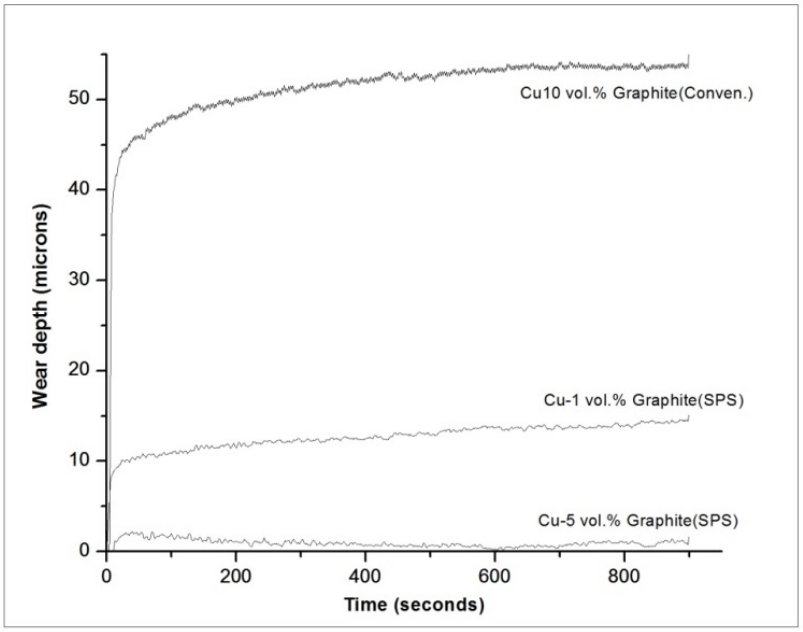

Figure 11: Variation of wear depth with time for Cu-10 vol. % Graphite (conventionally sintered) Cu-1 vol. % Graphite (SPS) & Cu-5 vol. % Graphite (SPS)

Figure 12 shows the SEM images of worn surfaces of SPS Cu-5 vol% graphite, SPS Cu-1 vol% graphite, conventionally sintered Cu-10 vol% graphite and pure copper samples.

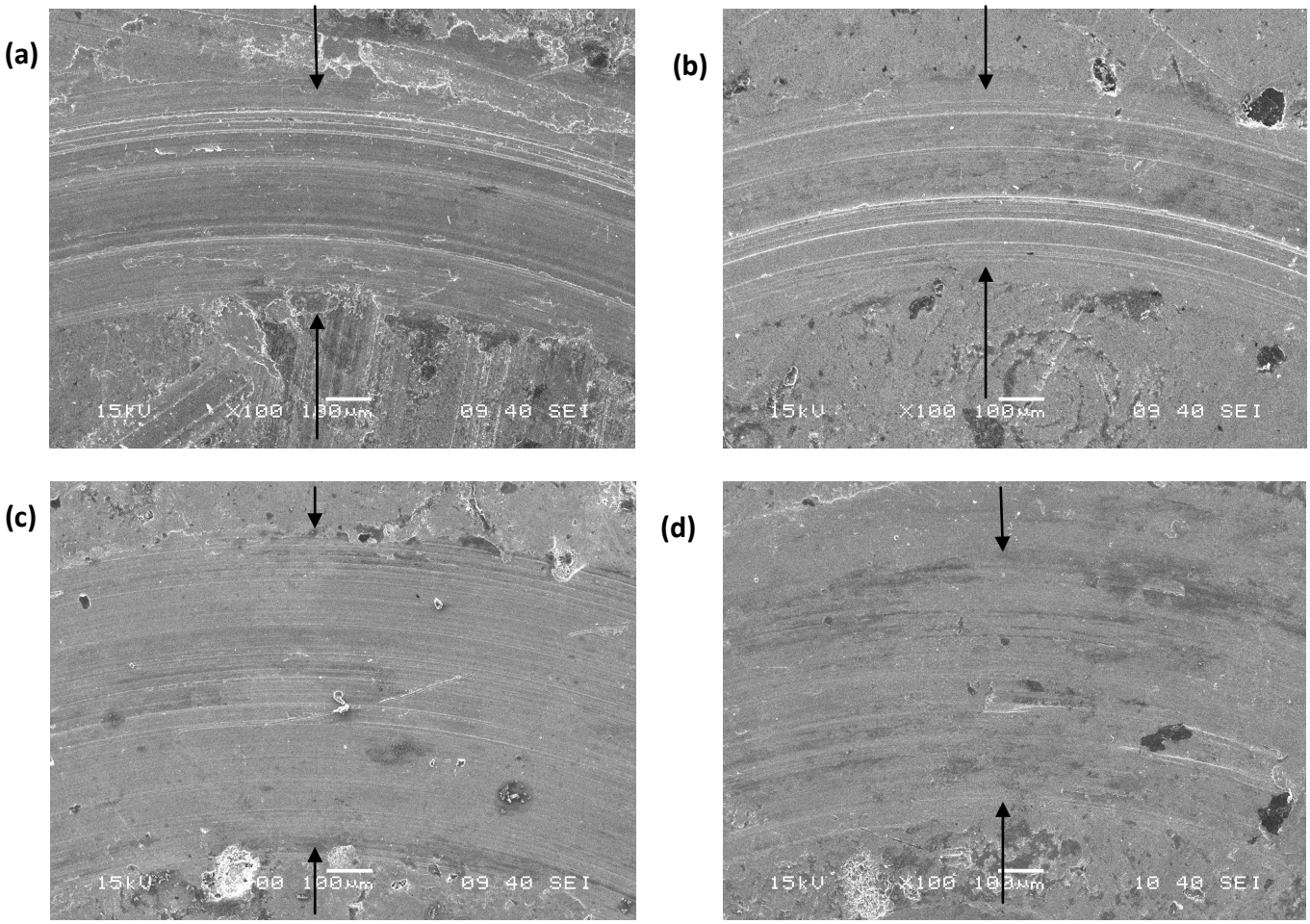

Figure 12: SEM images of worn surfaces of (a) SPS Cu-1 vol. % graphite, (b)SPS Cu-5 vol. % graphite, (c) Conventionally Sintered Cu-10 vol. % graphite, (d) Pure Copper samples

From the micrographs we can see that the wear depth decreases as per the following trend:

Pure Cu > Cu-10 vol% graphite (CS) > Cu-1 vol% graphite (SPS) > Cu-5 vol% graphite (SPS)

Graphite adheres to the wear surface, and a solid self-lubricating film comes into being on the wear surface. The contacts between metal and metal are transformed into the contacts between graphite film and metal or graphite film and graphite film. Therefore, the wear properties of Cu–graphite composites are greatly improved in comparison with those of pure copper.

CHAPTER 5

CONCLUSIONS

The following conclusions were drawn after analysing the results obtained from our project:

1. Copper-graphite composite has been successfully fabricated by powder metallurgy process using conventional and spark plasma sintering techniques.
2. XRD study shows the existence of both copper and graphite (carbon) phases along some copper oxide in conventionally sintered samples. The SPS samples were devoid of any oxide inclusions because of the vacuum conditions.
3. SEM study suggests proper bonding between matrix and reinforcement along their interface.
4. Density study shows an increasing trend with increase in content of graphite.
5. Hardness of Cu-graphite composite decreases with increase in amount of graphite due to soft nature of graphite.
6. Wear studies of the composite samples indicate decrease in wear depths with increasing volume % of graphite due to the increase in thickness of the smeared graphite layer on the surface.
7. In general, the samples prepared by spark plasma sintering showed superior properties compared to those prepared by conventional sintering.

CHAPTER 6

SCOPE FOR FUTURE WORK

- To improve the interfacial bonding between copper and graphite by the use of pitch coke.

- In-depth wear study, i.e., effect of load, coefficient of friction, wear rate, wear volume, wear mechanism, etc. can be done.

- Electrical conductivity tests can also be carried out to study the effect of addition of graphite on the inherent electrical conductivity properties of copper.

- Other sintering techniques like microwave sintering, hot pressing techniques, etc can be used for the fabrication of the composite.

- Different sintering parameters like sintering temperature, time, compaction pressure, heating rates, etc can be optimized.

CHAPTER 7

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